Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

In situ conversion of MOG to crystalline MOF: A case study on solvent-dependent gelation and crystallization

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CCDC Numbers for crystals structures are CCDC 2182946, 2182948

Experimental section

General methods

All the chemicals such as pyrene, $NaIO_4$, $RuCl_3$ and the required other metal salts were purchased from local chemical suppliers and used without purification. FTIR spectra were recorded with a Perkin Elmer Instrument Spectrum Rx Serial No. 73713. ^1H NMR spectra were recorded on a BRUKER-AC 400 MHz spectrometer. Powder XRD patterns were recorded with a BRUKER-AXS D8 ADVANCE diffractometer.

FESEM study

The morphologies of the gel and crystalline materials were characterized by a field emission scanning electron microscope FEI NOVA NANOSEM 450. Samples were prepared by drop casting the gelatinous material or sol on the aluminum foils and then dried in air for 12 h. Au-coating was done on the samples before starting the analysis.

TEM analysis

TEM analysis of the gel material had been characterized by Transmission Electron Microscope TEM-FEI-TECNAI G^2 20S-TWIN, Type-5022/22. TEM analysis had been carried out by drop casting the gel materials on carbon coated Cu-grid and followed by air dry.

Polarized Optical Microscope (POM)

The polarizing optical light micrographs for the samples were obtained from a LEICA DMLM (Germany) optical microscope by transmitted light under crossed Nicol and fitted with JVC-KY-F550E imaging system. Little amount of gelatinous sample or sol or crystalline material was placed on the microscope before the analysis.

Rheological measurements

For the **Zn-MOG**, rheological measurements were carried out on an Anton Paar MCR 102 rheometer using 25 mm diameter parallel plate geometry with a constant tool gap of 1 mm. The gel sample was kept on the lower plate and a stress amplitude sweep experiment was performed at a constant frequency at 25 °C to obtain the storage or elastic modulus or G′, and the loss or viscous modulus or G″. The frequency sweep measurements were carried out at a constant stress in the linear viscoelastic range.

Synthesis of Zn-MOG

The molecule H_4NCA (10.50 mg, 0.025 mmol) was dissolved in 2mL of DMF and $ZnSO_4$ (14.40 mg, 0.050 mmol) was dissolved in 2mL of water and then these two solutions were mixed in a tube. After that the tube was sealed properly and it was kept in an oven at 95°C. After 12 hours, **Zn-MOG** was obtained as white coloured opaque viscous material. Xerogel of **Zn-MOG** was prepared by drying the gel in air. IR of the xerogel of **Zn-MOG** (cm^{-1}, KBr): 3489.24, 3106.63, 1686.99, 1645.18, 1565.21, 1528.05, 1452.50, 1438.11, 1418.10, 1375.40, 1354.58, 1106.41, 933.43, 747.75, 726.85, 684.36, 540.54, 514.40.

Synthesis of CR1

This material was synthesized following the above procedure but the solution in the sealed tube was kept in the oven for 5-6 days to obtain crystalline materials. Yield.- 30%; IR (cm^{-1}, KBr): 3551.94, 3311.33, 1667.51, 1625.92, 1580.86, 1514.31, 1427.26, 1348.44, 1332.88, 1106.18, 930.16, 890.86, 820.31, 718.76, 686.17, 553.52, 532.08.

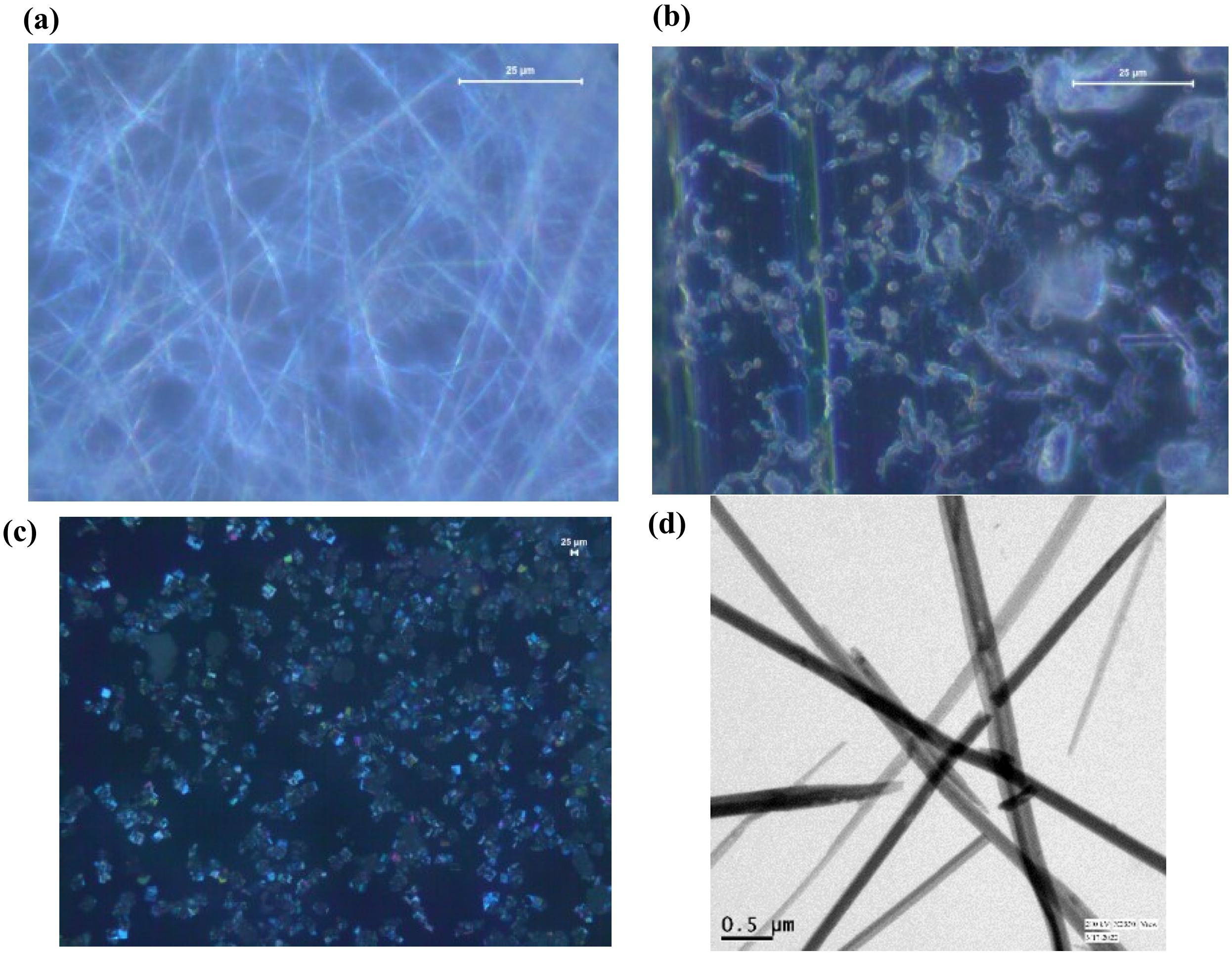

Fig. S1. POM images of (a) xerogel of the **Zn-MOG**, (b) the intermediate state between gel and crystalline phase, (c) crystals of **CR1**, d) TEM images of **Zn-MOG**.

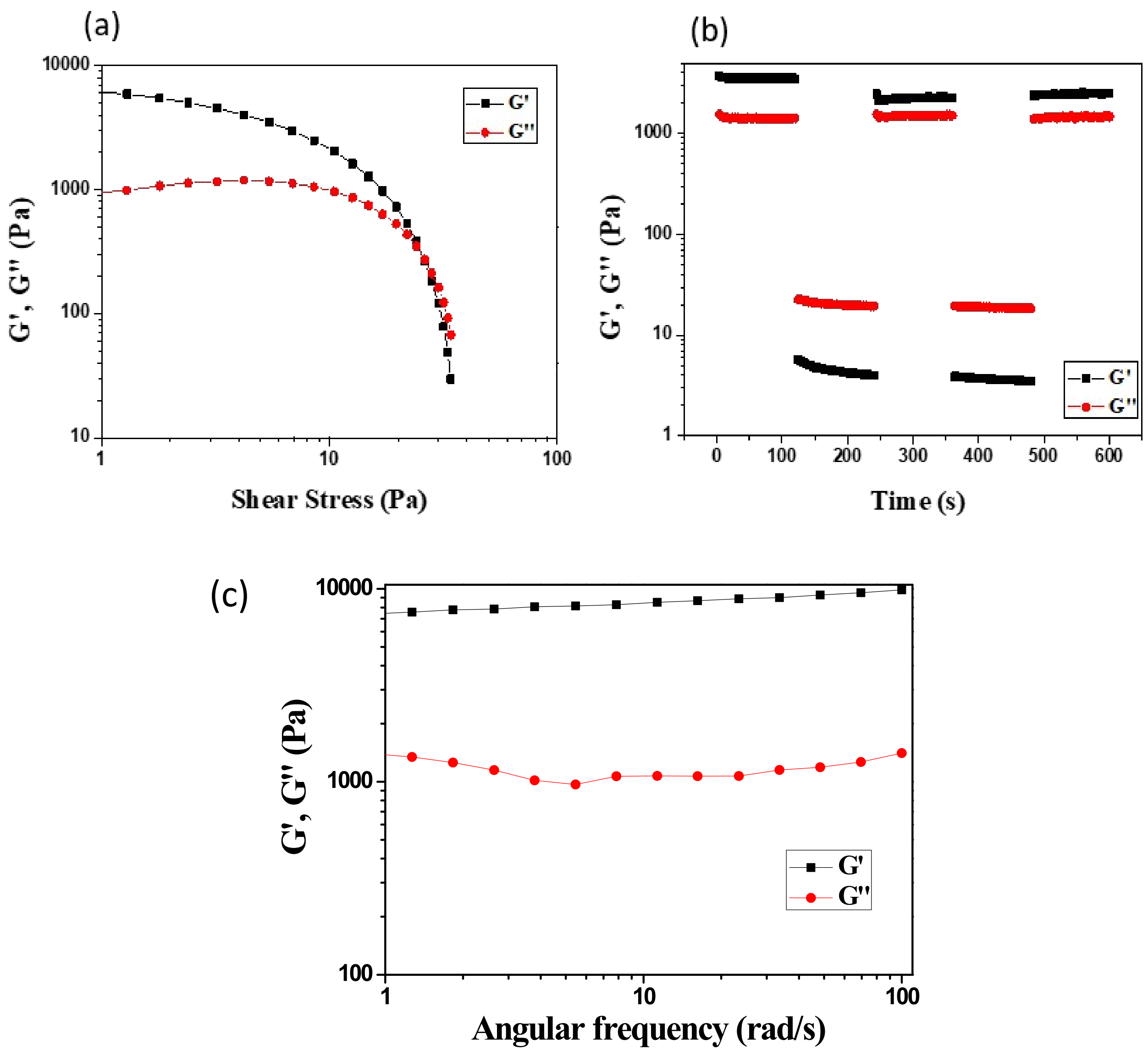

Fig. S2. Rheological experiments for **Zn-MOG**: (a) Variation of storage modulus (G′) and loss modulus (G″) with shear stress; (b) thixotropy-loop test via continuous step-strain measurements; (c) variation of storage modulus (G′) and loss modulus (G″) with frequency in the rheological experiments for **Zn-MOG**.

Synthesis of CR2

This material was synthesized following the similar procedure as described for **Zn-MOG** with the exception of the solvent-system which was DMA-H_2O instead of DMF-H_2O and pure colorless crystalline materials of **CR2** were obtained after heating the solution for 24 hours at the above-mentioned temperature. Yield.-75%; IR (cm^{-1}, KBr): 3218.86, 1602.95, 1556.89, 1514.42, 1424.32, 1343.45, 1146.81, 1102.99, 1055.11, 927.27, 858.99, 822.64, 768.23, 716.86, 597.55, 535.04.

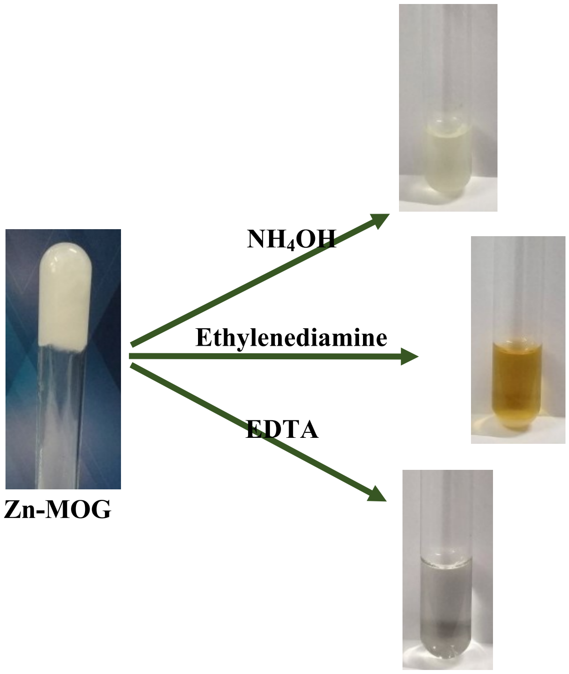

Fig. S3. Illustrations for gel-sol transformation of **Zn-MOG** by the addition of external chemical stimuli such as NH$_4$OH, ethylenediamine and EDTA.

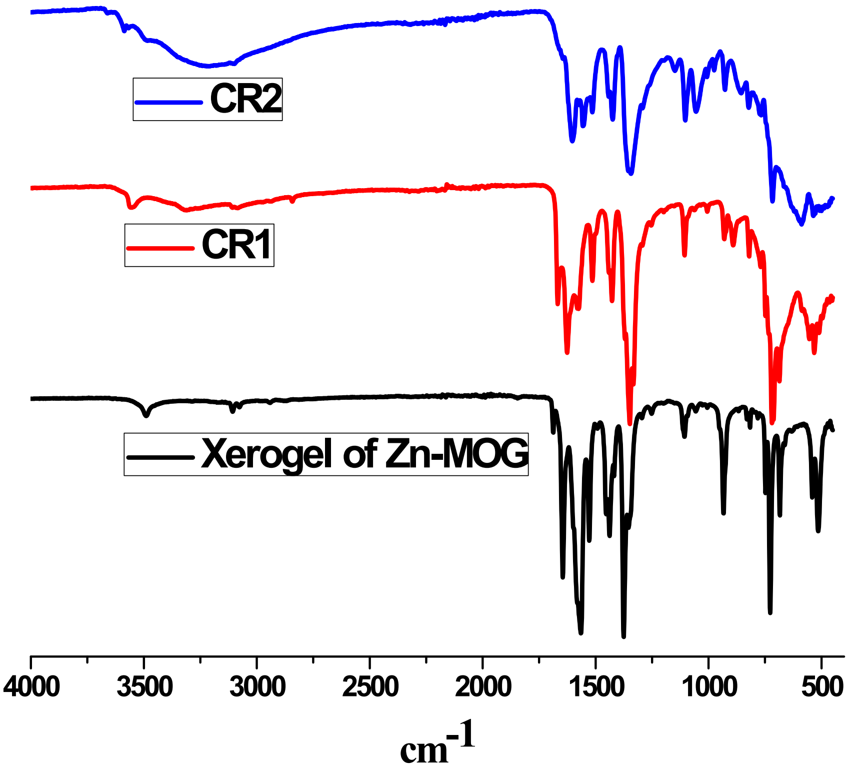

Fig. S4. IR spectra of xerogel of **Zn-MOG**, **CR1** and **CR2**.

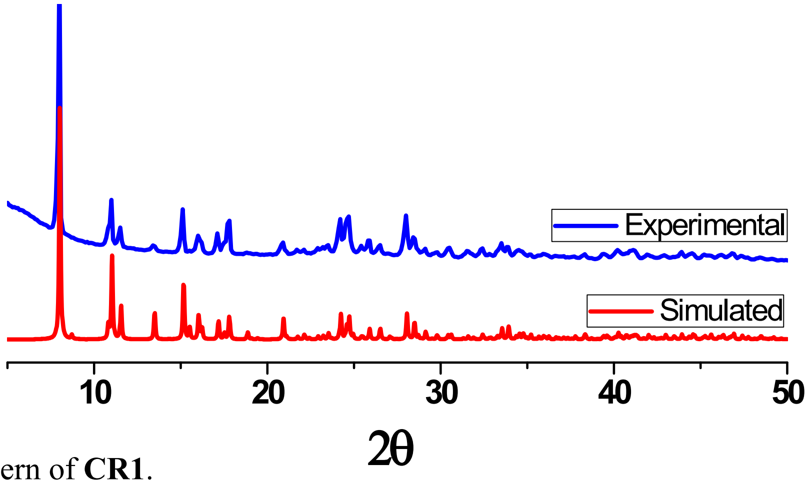

Fig. S5. PXRD pattern of **CR1**.

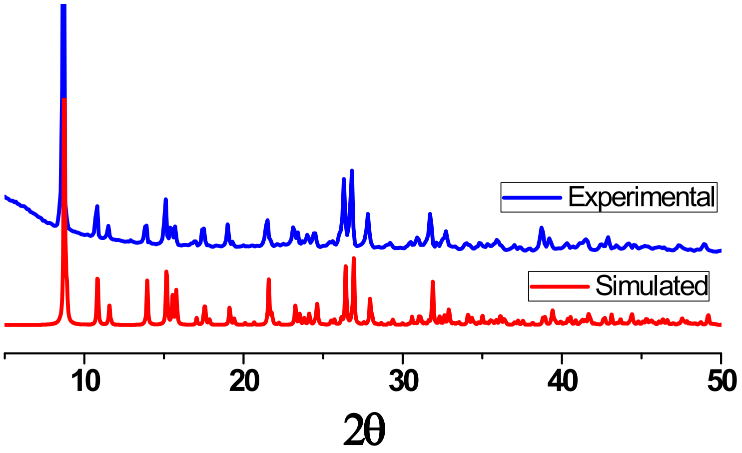

Fig. S6. PXRD pattern of **CR2**.

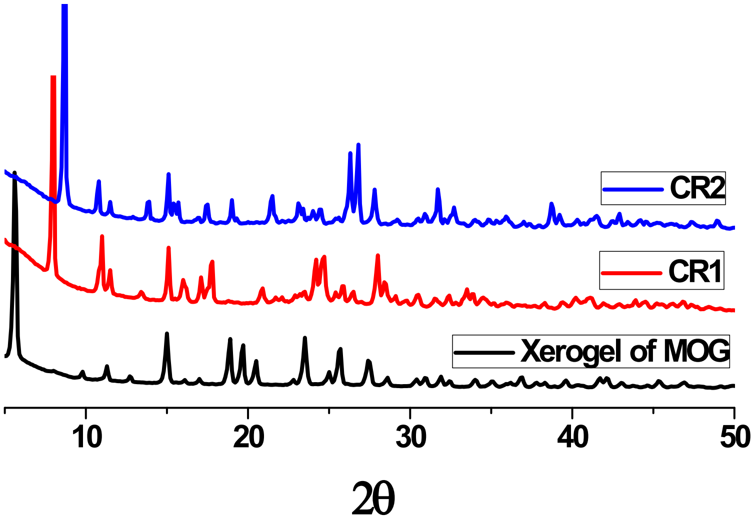

Fig. S7. PXRD patterns of the xerogel of **Zn-MOG** (black), **CR1** (red) and **CR2** (blue).

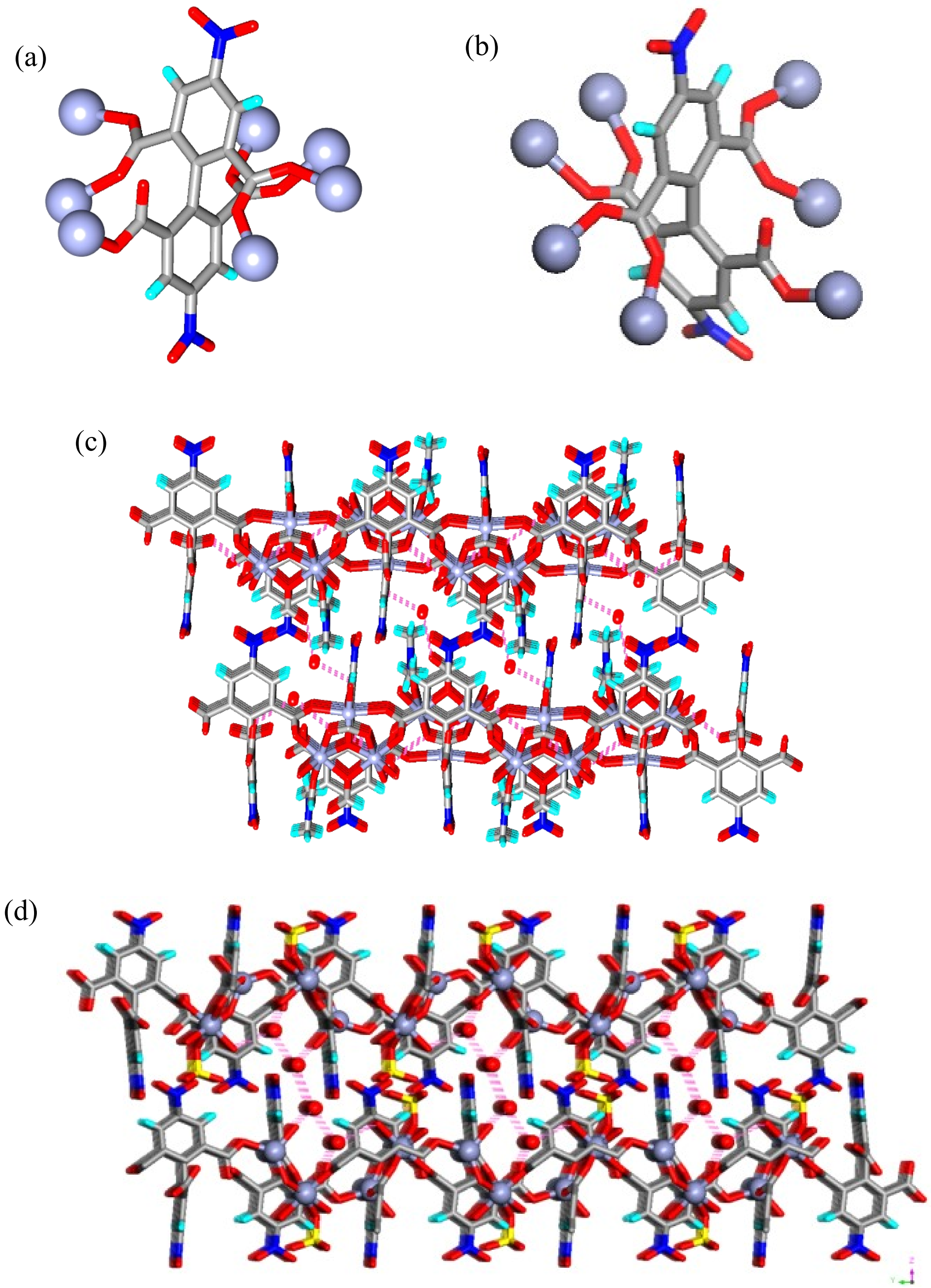

Fig. S8. Coordination mode of NCA in (a) **CR1** and (b) **CR2**; Hydrogen bonding between the 2D layers via water-bridging in (c) **CR1** and (d) **CR2**.

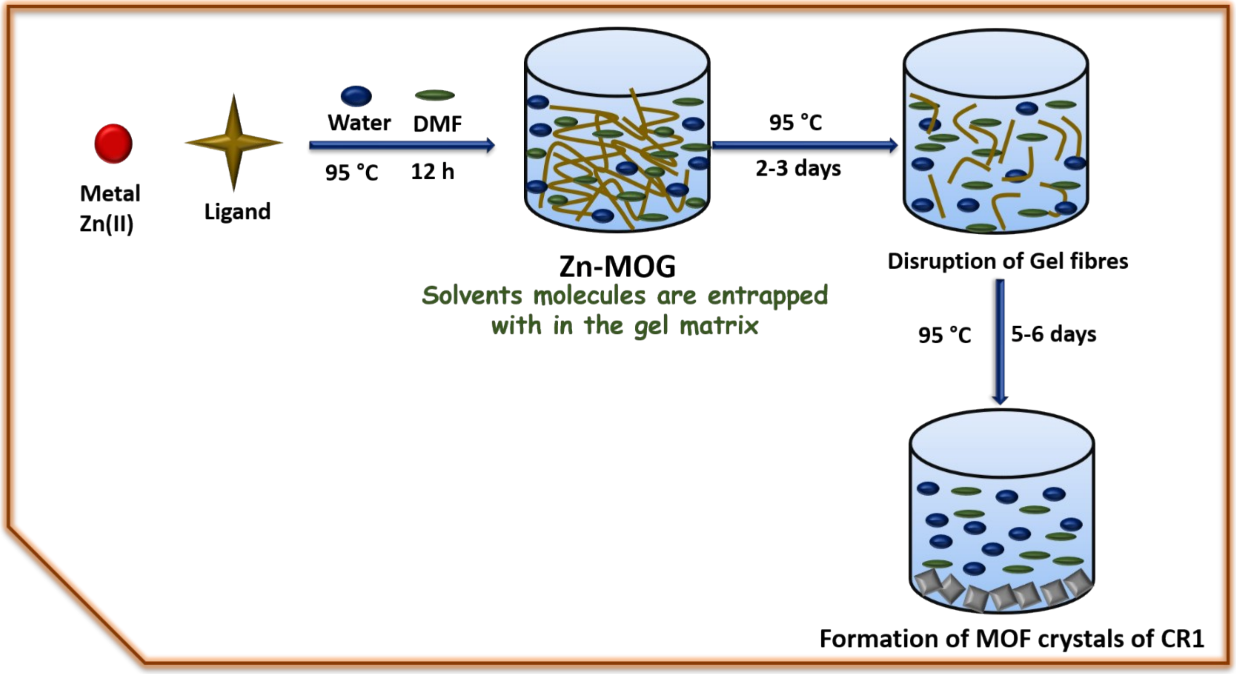

Fig. S9. A schematic mechanism for the conversion of **Zn-MOG** to **CR1** MOF crystals

Table S1. Crystallographic Parameters for **CR1** and **CR2**

Complex	**CR1 (**2182946)	**CR2** (2182948)
Formula	$C_{20}H_{25}N_3O_{22}Zn_3$	$C_{32}H_{28}N_4O_{48}SZn_6$
Mol.Wt.	855.46	1660.86
T (K)	293(2)	293(2)
System	Orthorhombic	Orthorhombic
Space group	$Pna2_1$	Pnnm
a (Å)	22.013(3)	11.683(5)
b (Å)	11.4171(16)	20.206(13)
c (Å)	11.6725(17)	11.397(6)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	2933.59(7)	2690(3)
Z	4	2
D(g/cm^3)	1.9076(5)	2.050
R_1 [$I > 2\sigma(I)$]	0.0781	0.0397
wR_2 (on F^2, all data)	0.1836	0.1237

Crystal structure determination. Single crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature (293 K) by the hemisphere method. The structures were solved by direct methods and refined by least-squares methods on F^2 using SHELX-2014.[1] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions and refined using a riding model.

1. Sheldrick, G. M. *SHELXL-2014*; University of Göttingen and Bruker AXS, Karlsruhe, Germany, **2014**.